I. AN OXIDATION-REDUCTION CYCLE IN EMULSION POLYMERIZATION SYSTEMS

II. INTERACTION OF INSOLUBLE POLYMERIC ELECTROLYTES WITH ACIDS AND BASES

BY

THOMAS JAMES SWOBODA

B.S., University of Wisconsin, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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I. AN OXIDATION-REDUCTION CYCLE IN EMULSION POLYMERIZATION SYSTEMS

The conditions under which synthetic polymers are prepared markedly affect their physical and chemical properties. In certain instances a superior product is obtained when the polymerization is carried out at low temperatures, but the rate of reaction may be so slow that the process is impractical. For a polymerization taking place through a free radical mechanism, the over-all rate of reaction depends, among other things, upon the concentration of free radicals present. While at reduced temperatures the thermal decompositions of free radical producing compounds, such as benzoyl peroxide, are too slow to maintain optimum free radical concentrations, it is found that the formation of free radicals can be considerably hastened by the presence of ferrous iron. Since ferrous iron is a reducing agent and the peroxide an oxidizing agent, the combination is said to constitute a "Redox" system, and the increased catalytic effect of the peroxide is said to be the result of reduction activation.

A variety of highly effective "Redox recipes" for the preparation of various polymers, such as the copolymer of butadiene and styrene, have been devised by polymerization technologists. These recipes are complex reaction systems which involve a variety of substances in addition to the monomer, peroxide, and iron. A typical recipe, consisting only of those reagents which are necessary and sufficient, is: 20 g. monomer, 40 g. water, 0.1 g. benzoyl peroxide, 0.1 g. ferric ammonium sulfate, 0.1 g. sorbose, 0.1 g. sodium pyrophosphate, 1.0 g. sodium stearate. The work reported here was undertaken to establish the functional role of each of the ingredients in these recipes.

As a result of this investigation, it appears that the following is a proper description of the behavior of these recipes. The iron in the emulsion is originally present as ferric iron which is tied up for the most part as a pyrophosphate complex

in the water. But ferric iron can be reduced by sorbose or some other reducing sugar to form ferrous iron, a large portion of which also remains as a pyrophosphate complex in the water. However, limited amounts of both ferrous and ferric iron will tend to pass into the monomer cores of the emulsion micelles, presumably as the stearate salts, since ferrous and ferric stearates are monomer soluble compounds. The distribution between the phases will occur in accordance with the usual laws governing distribution of solutes between immiscible solvents. In the monomer cores the ferrous iron can react with the monomer soluble peroxide to form free radicals and ferric iron. The free radicals start the polymerization going and the ferric iron ultimately passes back into the water.

Thus these reduction activated polymerization catalysts are capable of maintaining a rapid but controlled production of free radicals in an environment of high monomer concentration even at reduced temperatures. Sodium stearate is used as an emulsifying agent, but it does more than promote emulsification, since it also renders the iron salts monomer soluble. Omitting any of the reagents mentioned above or replacing the soap by a cationic emulsifying agent which is incapable of solubilizing the iron in the monomer disrupts the smooth operation of the recipe.

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II. INTERACTION OF INSOLUBLE POLYMERIC ELECTROLYTES WITH ACIDS AND BASES

Insoluble polymeric electrolytes, such as wool or nylon fibers, when placed in aqueous solutions of acids or bases, absorb ions to definite equilibrium amounts. It is generally agreed that for a polyamide such as nylon, this absorptive process involves the formation of salt linkages with the carboxyl and amino end groups of the polymer. The significance of the fibrous character of the insoluble polymeric electrolytes has been clearly established by Gilbert and Rideal (2), who set the behavior of these electrolytes apart from that of the soluble proteins.

Considerations involving the electrostatic fiber potential lead to the assumption that anions and cations are absorbed in stoichiometrically equivalent amounts. Titration equations which quantitatively describe the absorption process can be obtained by equating the chemical potential of ions absorbed

by the fibers with that of the ions in the solution. These titration equations relate the amount of various ions absorbed to the *p*H of the equilibrium solution.

In the present study, titration equations have been derived for the absorption of either a monovalent acid or a monovalent base. Fibers possessing an excess of either carboxyl or amino end groups, or an equal number of each, have been considered. The absorption of sodium hydroxide by nylon fibers containing a larger number of carboxyl than amino end groups was investigated experimentally. This absorption is one of the instances in which the absorption process is divided into two distinct absorption regions, each characterized by a substantially different absorption reaction. A complete absorption curve from approximately zero to total saturation of the fibers was obtained. The complexities of this two-step absorption curve were successfully interpreted by the titration equations derived. By means of appropriate graphs based on these equations, estimates of the equilibrium coefficients for the absorption reactions of each of the two regions of absorption were obtained. Similarly, values for the number of carboxyl and amino end groups per gram of fiber were obtained which agree well with values offered by other workers who employed entirely independent methods.

In much of this work, radioactive tracer techniques which employed the sodium isotope, (Na^{22}), were used to measure the extremely small amounts of base absorbed by the fibers. The use of these techniques in the study of absorption by fibers is unique.

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